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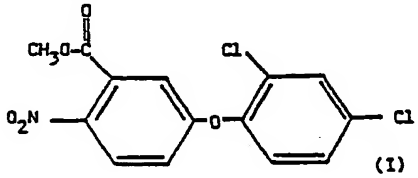
(71) Applicants
Lilly Industries Limited,
Henrietta House,
Henrietta Place, London
W.1., England
(72) Inventors
Jean Marc Beraud, James
Leslie Glasgow, George
Skylakakis
(74) Agent
K. W. H. McVey

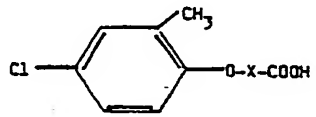
(54) Herbicides

(57) The selective control of weeds in post-emergence treatment of cereal crops employing a combination of a compound of formula I



(I)

and a compound of formula II



(II)

wherein X is —CH(CH$_3$)—, —CH$_2$— or —(CH$_2$)$_3$—
the treatment being shown to be synergistic, particularly in controlling the problematic weed species *Matricaria spp.*

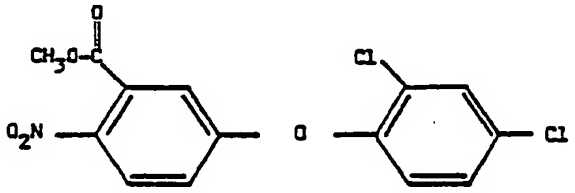
GB 2 031 279 A

SPECIFICATION
Herbicides

The invention relates to a method of combating weeds in cereal crops and to herbicidal formulations for use in such method.

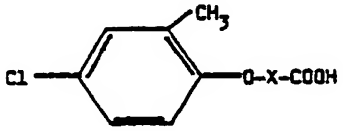
Heretofore, the broadleaf weed species *Matricaria* spp has proved particularly resistant to conventional herbicides, causing much damage to winter and spring cereal crops such as wheat, barley, oats and rye. We have now found that by using a combination of particular known herbicides this weed species is controlled to a surprisingly high level, synergism, in accordance with the well-known "Colby Equation" (*Weeds*, 15, 20—22, 1967), being observed. Additionally, control of other problematic weed species has been found to be very satisfactory when using the combination, synergism again being observed in several cases.

Thus, according to the present invention a method of combating weeds in a cereal crop locus comprises applying to said locus, post emergence the crop, a compound of formula I,



(I)

and one or more compounds of formula II,



(II)

wherein

X is —$CH(CH_3)$—, —CH_2— or —$(CH_2)_3$—; where a compound of formula II, in which X is —$CH(CH_3)$—, is employed, the compound of formula I being applied at a rate of 0.25 to 3.0 kg/ha and the compound of formula II being applied at a rate of 0.5 to 3.0 kg/ha; where a compound of formula II, in which X is —CH_2—, is employed, the compound of formula I being applied at a rate of 0.7 to 2.0 kg/ha, and the compound of formula II being applied at a rate of 0.7 to 3.0 kg/ha, and where a compound of formula II, in which X is —$(CH_2)_3$—, is employed, the compound of formula I being applied at a rate of 0.25 to 3.0 kg/ha and the compound of formula II being applied at a rate of 0.1 to 3.5 kg/ha, the crop being other than spring wheat where a single compound of formula II, wherein X is —$CH(CH_3)$—, is employed.

In general, the compound of formula I is applied at a rate of from 0.7 to 2.0 kg/ha and the compound(s) of formula II at a rate of from 0.7 to 3.0 kg/ha.

The compound of formula I is known as bifenox, the preparation thereof being described in United Kingdom Patent Specification No. 1,232,368 and its use as a herbicide being described in *Proc. N. E. Weed Sci Conf.* 1973, *27*, 31.

The compound of formula II, wherein X is —$CH(CH_3)$—, is known as mecoprop.

The compound of formula II, where X is —CH_2—, is known as M.C.P.A.

The compound of formula II, wherein X is —$(CH_2)_3$—, is known as M.C.P.B.

Mecoprop, M.C.P.A., M.C.P.B., their salts and esters, their manufacture and their herbicidal properties are well documented in the literature.

The compounds of formula II may be employed in free acid form or in a salt or ester form which is non-phytotoxic to cereals. As examples of salts forms may be given the alkali-metal, e.g. sodium and potassium, salt forms and the ammonium, alkylammonium and alkanolammonium salt forms, e.g. the ethanolammonium salt form. As examples of ester forms may be given the lower, e.g. C_{1-8}, alkyl ester forms, e.g. the methyl and octyl ester forms. The use of such salts and ester forms is embraced by the present invention.

In the method of the present invention, the compound of formula I (bifenox) is preferably employed at an application rate of from 0.7 to 1.5 kg/ha and more preferably at a rate of about 0.75 to 1.0 kg/ha. The compounds of formula II, wherein X is —$CH(CH_3)$— or —$(CH_2)_3$—, i.e. mecoprop or M.C.P.B., is preferably employed at an application rate of from 1.0 to 2.0 kg/ha. The compound of f rmula II, wherein X is —CH_2—, i.e. M.C.P.A., is preferably employed at an application rate of from 0.7 to 1.5 kg/ha and more preferably at a rat f about 0.75 to 1.0 kg/ha.

The weight ratio of the compound of formula I to the c mpound(s) of formula II is generally in th

range of from 1:4 to 3:1. Where the bifenox is employed together with mecoprop or M.C.P.B., the weight ratio of the former to the latter is preferably in the range from 1:3 to 1.5:1, more preferably about 1:2. Where the bifenox is employed together with M.C.P.A., the weight ratio of the former to the latter is preferably in the range of from 1:2 to 2:1, more preferably about 1:1.

In the case of the compounds of formula II, the above weights and ratios are based on the acid equivalent thereof if a salt or ester is employed.

The method of the present invention is preferably carried out when the crop is between the one leaf stage and appearance of the second node.

The preferred crops for treatment by the method of the present invention are winter wheat, spring barley and winter barley.

The compound of formula I and the compound(s) of formula II may be applied together or separately. If the latter, the time period between applications is preferably short, say one day or less. It is by far preferred, however, for the compounds to be applied simultaneously as a single formulation. In order to simplify manufacture, storage and transport, herbicidal formulations will normally be produced in concentrate form intended for dilution in water to the degree necessary to enable the above application rates to be achieved. Such concentrate formulations may contain from 1 to 90%, preferably 15 to 85%, by weight of active ingredients associated with one or more inert, non-phytotoxic, carriers therefor. Such formulations will usually be in the form of a wettable powder, an emulsifiable concentrate or an aqueous suspension or solution.

Herbicidal formulations form a further aspect of the present invention. Thus, there is provided a herbicidal formulation to be used in the method of the invention, after dilution if appropriate, and comprising a compound of formula I and one or more compounds of formula II, or a salt or ester thereof, in a weight ratio range of from 1:4 to 3:1 (based on the acid equivalent of the compound(s) of formula II) together with a non-phytotoxic diluent or carrier. The preferred weight ratio ranges are as given above.

As a further separate aspect of the present invention, there is provided a herbicidal formulation comprising a compound of formula I, stated above, together with a compound of formula II, in which X is $—(CH_2)_3—$, or a salt or ester thereof, in a weight ratio range of from 1:4 to 3:1 (based on the acid equivalent of the compound of formula II), together with a non-phytotoxic diluent or carrier. Again, the preferred weight ratio ranges are as given above.

The herbicidal formulations of the present invention are intended to embrace not only the so-called concentrate formulation forms, but also ready-to-use dilute formulations such as tank mixes and application spray liquors. Such dilute formulations are generally produced by dilution down to the appropriate degree of concentrate formulations but, if desired, may be produced by the separate addition of appropriate amounts of the individual components to an appropriate diluent or carrier.

Turning, however, to the concentrate formulations, wettable powders comprise an intimate mixture of the active ingredients, one or more inert carriers and one or more appropriate surfactants. The inert carrier may be chosen from the attapulgite clays, the montmorillonite clays, the diatomaceous earths, kaolins, micas, talcs and purified silicates. Effective surfactants may be found among the sulphonated lignins, the naphthalene sulphonates and condensed naphthalene sulphonates, the alkyl succinates, the alkylbenzene sulphonates, the alkyl sulphates and non-ionic surfactants such as ethylene oxide adducts of phenol. Illustrative wettable powders are those having the following composition:

WETTABLE POWDERS

	% by weight
Compound of formula I	1 to 73
Compound of formula II*	1 to 79
Surfactant(s)	1 to 10
Dispersing Agent	0 to 10
Anticaking Agent	0 to 10
Inert carrier(s)	to 100

*based on acid equivalent

Emulsifiable concentrates comprise the active ingredients dissolved in one or more suitable solvents, together with a surfactant. As examples of solvents may be given alkyl substituted benzenes, o-chlorotoluene, heavy aromatic naphthalenes, glycol ethers and cyclic ketones. Illustrative emulsifiable

concentrates are those having the following composition:

EMULSIFIABLE CONCENTRATES

	% weight/volume
Compound of formula I	1 to 55
Compound of formula II*	1 to 60
Surfactant(s)	2 to 10
Co-solvent	0 to 40
Solvent	to 100

*Based on acid equivalent

Aqueous suspensions and solutions comprise the active ingredients suspended or dissolved in water together with any desired surfactants, thickening agents, antifreezing agents or preservatives. Suitable surfactants may be chosen from those mentioned above in connection with wettable powders. Thickening agents, if used, are normally chosen from appropriate cellulose materials and natural gums, whilst glycols will generally be used when an antifreezing agent is required. Preservatives may be chosen from a wide range of materials such as the various paraben antibacterials, phenol, *o*-chlorocresol, phenyl mercuric nitrate and formaldehyde. Illustrative aqueous suspensions are those having the following composition:

AQUEOUS SUSPENSIONS

	% weight/volume
Compound of formula	4 to 59
Compound of formula II*	5 to 65
Wetting Agent	0 to 10
Dispersing Agent	0 to 6
Thickening/Suspending Agent	0 to 5
Antifreeze Agent.	0 to 15
Preservative	0 to 2
Water	to 100

*Based on acid equivalent

The aqueous suspension and wettable powder formulations are preferred for use in the method of the present invention, giving significantly lower phytotoxicity to the cereal crop than the emulsifiable concentrate formulations.

The following Examples further illustrate the inventions. In all Examples, the amount of mecoprop, M.C.P.A. and M.C.P.B. used is based on the acid equivalent.

EXAMPLES 1 TO 5

The following wettable powders were prepared, in each case having the ingredients shown:

	% by weight
(1) Bifenox	20
M coprop (potassium salt)	40

Sodium lauryl sulphate	3
Sodium lignin sulphonate	3
Precipitated silica	8
Kaolin	to 100

	% by weight
(2) Bifenox	20
Mecoprop (Sodium salt)	27
Ethoxylated alkyl phenol	4
Lignosulphonate	3
Fumed Silica	6
Attapulgite	to 100

	% by weight
(3) Bifenox	10
Mecoprop (diethanolamine salt)	25
Sodium salt of condensed naphthalene sulphonic acids	6
Precipitated silica	10
Sodium alumino silicate	to 100

	% by weight
(4) Bifenox	30
M.C.P.B. (sodium salt)	45
Sodium lauryl sulphate	2
Sodium lignin sulphonate	3
Precipitated silica	5
Montmorillonite	to 100

	% by weight
(5) Bifenox	30
M.C.P.A. (sodium salt)	30
Sodium lauryl sulphate	2
Sodium lignin sulphonate	3
Precipitated silica	5
Montmorill nite	to 100

In each Example, the active ingredients were carefully blended with the specified exipients in conventional mixing equipment. The blend was then further milled in a fluid energy mill to a size range of from 1 to 10 microns.

EXAMPLES 6 TO 10

The following emulsifiable concentrates were prepared having the constituents shown below:

	% by weight/ by volume
(6) Bifenox	15
Mecoprop	30
Calcium dodecylbenzone sulphonate	3
Alkyl phenoxypolyoxyethylene ethanols	3
Isophorone	20
Xylene	to 100

	% by weight/ by volume
(7) Bifenox	15
Mecoprop ester	20
Alkyl aryl sulphonate	4
Polyoxyethylene triglyceride	4
Cyclohexane	20
Orthochlorotoluene	to 100

	% by weight/ by volume
(8) Bifenox	10
Mecoprop	25
Amine salt of dodecylbenzene sulphonic acid	3
Polyoxyethylene sorbital fatty esters	4
Isophorone	15
Heavy aromatic naphtha	to 100

	% by weight/ by volume
(9) Bifenox	20
M.C.P.B. (mixed butyl esters)	30
Calcium dodecylbenzene sulphonate	3
Alkyl phenoxypolyoxyethylene ethanols	4
Isophorone	30
Orthochlorotoluene	to 100

	% by weight/ by volume
(10) Bifenox	20
M.C.P.A.	20
Calcium dodecylbenzene sulphonate	3
Alkylphenoxypolyoxyethylene ethanols	4
Isophorone	30
Orthochlorotoluene	to 100

The active ingredients were added to the appropriate solvent(s) with stirring and optional heating to facilitate dissolution of the active materials. The surfactants were then added. The solutions were then filtered to remove insoluble impurities.

EXAMPLES 11 TO 13

The following aqueous suspensions were prepared having the constituents shown below:

	% by weight
(11) Bifenox	30
M.C.P.A. (amine salt)	30
(Ethyl)hydroxyethyl cellulose	0.2
Lignin sulphonate	3
Propylene glycol	2
Water	to 100

	% by weight
(12) Bifenox	20
M.C.P.B. (amine salt)	35
Hydroxyethyl cellulos	0.2
Amine ethoxylate	3
Water	to 100

		% by weight
(13)	Bifenox	25
	Mecoprop (amine salt)	50
	Hydroxyethyl cellulose	0.5
	Phosphate ester	3
	Ethylene glycol	2
	Water	to 100

The following Examples serve to illustrate the synergistic effect demonstrated by the method of the invention.

EXAMPLE 14

Several field trials were carried out on winter wheat and one on spring barley on sandy and clay loam soils. Applications was made as tank mixtures with a knapsack sprayer at a volume of 300—800 l/ha. The crop stage at application varied from the start of tillering to the stage at which the second node was visible. Visual assessments of herbicidal activity were made from 2 to 15 weeks after application using the Barratt and Horsfall (1945) rating system.

In the following table is set out the average of the results obtained in terms of percent control of the weed species *Matricaria* spp for the individual herbicides Bifenox, mecoprop and M.C.P.A. and for the tank mix combinations of Bifenox + mecoprop and Bifenox + M.C.P.A., there also being given the control value estimated by the Colby formula for additive effect. The concentrates from which the aqueous spray liquors were formed were Bifenox 80% wettable powder, mecoprop 55% aqueous solution and M.C.P.A. 40% aqueous solution.

TABLE

	Dosage Rate Kg/ha	% Control	
		Observed	Colby formula
Bifenox	1.0	16.1	N/A
Bifenox	1.5	25.5	N/A
Bifenox	2.0	40.3	N/A
M.C.P.A. (amine salt)	0.8	38.5	N/A
M.C.P.A. (amine salt)	1.6	64.8	N/A
Mecoprop (amine salt)	2.0	54.8	N/A
Bifenox + M.C.P.A. (amine salt)	1.0 + 0.8	85.1	48.4
"	1.5 + 0.8	93.4	54.2
"	2.0 + 1.6	95.3	79.0
Bifenox + mecoprop (amine salt)	1.0 + 2.0	86.0	62.1
"	1.5 + 2.0	89.0	66.3

Thus, from the above it can be seen that a genuine synergistic effect is observed when employing the method of the present invention.

Slight scorching of the crop was noted, which was subsequently out-grown.

As well as excellent control of the *Matricaria spp*, the following weed species were well controlled (greater than 80%) employing, in separate tests, the above combined tank mixes: *Anethum graveolens, Capsella bursa-pastoris, Centaurea cyanus, Fumaria officinalis, Lamium amplexicaule, Papaver rhoeas, Silene spp* and *Stellaria media.*

The Bifenox + M.C.P.A. combination additionally gave good control (greater than 80%) of the following weed species. *Anagallis arvensis, Chenopodium album, Polygonum aviculare Ranunculus arvensis, Ranuncules repens, Raphanus raphanistrum, Rumex crispus, Sinapis arvensis, Sonchus arvensis* and *Veronica hederifolia.*

The Bifenox + mecoprop combination additionally gave good control (greater than 80%) of *Galium aparine.*

EXAMPLE 15

The following greenhouse test was carried out to assess the efficacy of bifenox combined with M.C.P.B.

METHOD

Seeds: *Gallum aparine*

Matricaria recutita

Veronica persica

Planting: 0.5 cm depth. (*Matricaria sp* light covering)

Temperature/lighting: Greenhouse (cool)

Watering: when required

Fertilisation: none

Experiment design: randomised block (4 replicates)

Plot size treated: 10 x 10 cm pots

Soil texture: loam

Application equipment: single nozzle microsprayer, 50 cm band width, volume rate per area 50 ml per sq metre.

Weed Stage at Application: 3—5 true leaves.

In the following table is set out the average of the results obtained in terms of per cent control of the weed species, together with the control value estimated by the Colby formula. For the *Veronica persica* a visual control rating was made. For the other two species fresh weight of shoots was obtained. The bifenox from which the spray liquor was formed was an 80% wettable powder, the M.C.P.B. was a 48% aqueous solution, the combination being a tank-mix.

	Rate kg/ha	WEED SPECIES, % CONTROL					
		Matricaria Sp		*Galium aparine*		*Versonica persica*	
		Observed	Colby	Observed	Colby	Observed	Colby
Bifenox	0.75	56.5	N/A	62.5	N/A	77.0	N/A
M.C.P.B.	1.0	7.5	N/A	0.0	N/A	73.0	N/A
M.C.P.B.	1.5	2.4	N/A	0.0	N/A	78.0	N/A
Bifenox + MCPB	0.75 + 1.0	73.0	60.0	72.1	62.5	100.0	94.0
„	0.75 + 1.5	82.0	57.5	78.3	62.5	100.0	96.0

Thus, from the above, it can be seen that a genuine synergistic effect is observed when employing the method of the present invention.

EXAMPLE 16

This example further illustrates the synergistic effect demonstrated by the combination of bifenox + mecoprop when used for control of the broadleaf weed *Matricaria spp.*

Winter wheat was sown in France in October at a depth of 3 cm. and at a rate of 150 kg/hectare. The crop was allowed to grow without treatment until the following March, at which time the crop was at growth stage 4—5 (see *Plant Pathol., 3* 128—9, (1954)).

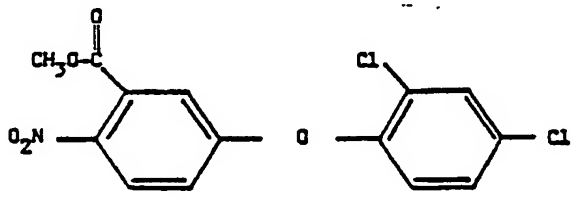
Bifenox and mecoprop were then applied separately and combined together as a tank mix and sprayed onto the area in which the crop was growing using a knapsack sprayer at a volume rate per hectare of 300 litres. Assessments, as weed control ratings, were made between 2 and 5 weeks after application.

TABLE

	Dosage rate g/hectare	*Matricaria* spp % control
Bifenox	1000	6
Bifenox	1500	15
Bifenox + Mecoprop	1000 + 2000	87
Bifenox + Mecoprop	1500 + 2000	88
Mecoprop	2000	50

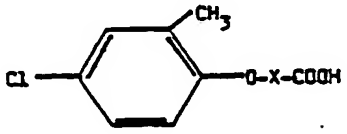
CLAIMS

1. A method of combating weeds in a cereal crop locus comprising applying to said locus, post emergence the crop, a compound of formula I,



(I)

and one or more comp unds of formula II



(II)

wherein

X is —CH(CH_3)—, —CH_2 or —$(CH_2)_3$—, where a compound of formula II, in which X is —CH(CH_3)—, is employed, the compound of formula I being applied at a rate of 0.25 to 3.0 kg/ha and the compound of formula II being applied at a rate of 0.5 to 3.0 kg/ha; where a compound of formula II, in which X is —CH_2— is employed, the compound of formula I being applied at a rate of 0.7 to 2.0 kg/ha and the compound of formula II being applied at a rate of 0.7 to 3.0 kg/ha, and where a compound of formula II, wherein X is —$(CH_2)_3$—, is employed the compound of formula I being applied at a rate of 0.25 to 3.0 kg/ha and the compound of formula II being applied at a rate of 0.1 to 3.5 kg/ha, the crop being other than spring wheat where a single compound of formula II, wherein X is —CH(CH_3)—, is employed.

2. A method according to claim 1, wherein the compound of formula I is applied at a rate of 0.7 to 2.0 kg/ha and the compound(s) of formula II at a rate of 0.7 to 3.0 kg/ha.

3. A method according to claim 1 or claim 2, wherein the compound of formula I is applied at a rate of from 0.7 to 1.5 kg/ha.

4. A method according to any one of claims 1 to 3, wherein, in the compound of formula II, X is —CH(CH_3)—.

5. A method of any one of claims 1 to 3, wherein, in the compound of formula II, X is —$(CH_2)_3$—.

6. A method according to claim 4 or 5, wherein the compound of formula II is applied at a rate of 0.7 to 1.5 kg/ha.

7. A method according to claim 6, wherein the compound of formula II is applied at a rate of from 0.75 to 1.0 kg/ha.

8. A method according to any one of claims 1 to 3, wherein, in the compound of formula II, X is —CH_2—.

9. A method according to claim 8, wherein the compound of formula II is applied at a rate of from 0.7 to 1.5 kg/ha.

10. A method according to claim 4 or 5, wherein the weight ratio of the compound of formula I to the compound of formula II is in the range of 1:3 to 1.5:1.

11. A method according to claim 8, wherein the weight ratio of the compound of formula I to the compound of formula II is in the range of 1:2 to 2:1.

12. A method according to any preceding claim, wherein the crop is a winter wheat spring barley or winter barley crop.

13. A method according to any preceding claim, wherein the crop is sprayed with spray application liquor formed by addition of water to an aqueous suspension or wettable powder formulation containing the compounds of formulae I and II.

14. A method according to any preceding claim, wherein the treatment of the crop takes place when the crop is at a stage between the one leaf stage and the appearance of the second node.

15. A method according to any preceding claim, wherein the compound of formula II is in a salt or ester form non-phytotoxic to cereal crops.

16. A method according to claim 1, substantially as hereinbefore described.

17. A herbicidal composition comprising a compound of formula I, stated in claim 1, and a compound of formula II, stated in claim 1, to be used at the rates and in the crops stated in claim 1, the weight ratio of the compound of formula I to the compound of formula II being in the range of 1:4 to 3:1.

18. A composition according to claim 17, wherein, in the compound of formula II, X is —CH(CH_3)—.

19. A composition according to claim 17, wherein, in the compound of formula II, X is —CH_2—.

20. A composition according to claim 17, wherein, in the compound of formula II, X is —$(CH_2)_3$—.

21. A composition according to any one of claims 17 to 20 in the form of an aqueous suspension or a wettable powder.

22. A herbicidal composition comprising a compound of formula I, stated in claim 1, together with a compound of formula II, stated in claim 1, in which X is —$(CH_2)_3$—.

23. A composition according to any one of claims 17 to 24, wherein the compound of formula II is in a salt or ester form non-phtotoxic to cereal crops.

24. A composition according to claim 17 to 22, substantially as hereinbefore described.

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